

REPORT DOCUMENTATION PAGE				<i>Form Approved</i> OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 20-07-2012		2. REPORT TYPE Briefing Charts		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE High-Performance Bio-Based Cyanate Esters with Low Moisture Uptake				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Guenthner, A.; Davis, M.; Reams, J.; Sahagun, C.; Mabry, J.				5d. PROJECT NUMBER	
				5f. WORK UNIT NUMBER 23031222	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB CA 93524-7401				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RQ-ED-VG-2012-244	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for public release; distribution unlimited. PA# 12604.					
13. SUPPLEMENTARY NOTES For presentation at the American Chemical Society 244 th Meeting, Philadelphia, PA 19-23 August 2012.					
14. ABSTRACT Key physical characteristics including density, packing fraction, moisture uptake, and as-cured dry glass transition temperature of cyanurate networks formed from bio-based cyanate esters synthesized from the natural product anethole were examined. The results showed that both equivalently high glass transition temperatures and lower moisture uptake compared to commercial materials could be achieved, though, for the non-optimal cure schedules studied, not in the same network. The most important factor in moisture uptake appeared to be the relation between the cure schedule and the glass transition temperature of the developing network. By optimizing these parameters, it may be possible to produce networks that exhibit both a higher glass transition temperature as well as lower moisture uptake compared to commercial materials.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON Dr. Joseph M. Mabry
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)
Unclassified	Unclassified	Unclassified			N/A



HIGH-PERFORMANCE BIO-BASED CYANATE ESTER RESINS WITH LOW MOISTURE UPTAKE

22 August 2012

Andrew Guenthner^{1*}

Matthew Davis,² Josiah Reams,³ Christopher Sahagun,³ Joseph Mabry¹

¹Aerospace Systems Directorate, Air Force Research Laboratory, Edwards AFB, CA

²Naval Air Warfare Center, Weapons division, China Lake, CA

³National Research Council / Air Force Research Laboratory

*Ph: 661/275-8020; e-mail: andrew.guenthner@edwards.af.mil



Outline



- Background / Motivation
 - About Cyanate Esters
 - Why Study Non-Petroleum Feedstocks for Cyanate Esters?
- Overview of Synthesis of Cyanate Esters from Anethole
- Properties of Anethole-Based Cyanate Esters
 - Effect of Segment Rigidity
 - Comparison to Common Dicyanate Esters
- Program Integration / Future Work



Acknowledgements: Strategic Environmental Research & Development Program (SERDP); Air Force Office of Scientific Research, Air Force Research Laboratory – Program Support; PWG team members (AFRL/RQRP)



More details in: Davis et al., *Journal of Polymer Science, Part A*, 2012, in press,, doi: 10.1002/pola.26218



AFRL Mission



*Leading the discovery, development, and integration
of affordable warfighting technologies for our air,
space, and cyberspace force.*

DISTRIBUTION A. Approved for Public Release. Distribution Unlimited (88ABW-2011-6418)

Distribution A. Approved for public release; distribution is unlimited





Cyanate Esters for Next-Generation Aerospace Systems



Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

Resin Viscosity
Suitable for
Filament
Winding / RTM

Compatible with
Thermoplastic
Tougheners and
Nanoscale
Reinforcements

High T_g

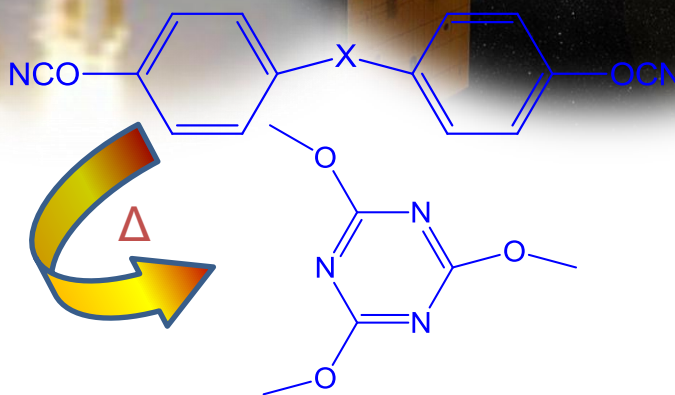
Onset of Weight Loss:
> 400 °C with High Char Yield

Ease of Processing

Resistance to Harsh Environments

Good Flame, Smoke, & Toxicity Characteristics

Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion



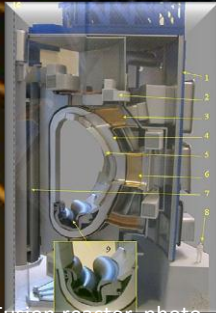


Cyanate Esters Around the Solar System



Our Solar System

- On Earth, cyanate ester / epoxy blends have been qualified for use in the toroidal field magnet casings for the ITER thermonuclear fusion reactor



Fusion reactor, photo courtesy of Gerritse ((Wikimedia Commons))

- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites
- The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers

Images: courtesy NASA (public release)



Why Bio-Based Cyanate Esters



- Materials qualification efforts are costly; developing bio-based materials that deliver both improved performance and decreased dependence on petroleum enables a higher and more robust return on investment
- Cyanate esters are generally easy to process; they do not require stoichiometric balance and form co-networks readily, hence they tolerate variation in monomer chemistry relatively well
- The superior flame, smoke, and toxicity characteristics of cyanate esters, the excellent adhesion and durability characteristics of the networks, and the very high selectivity of the reaction (which makes de-polymerization easier), all confer benefits from a sustainability perspective
- Bio-based feedstocks for cyanate esters are interesting because of the combinations of physical properties provided by structure of the molecules themselves, not just because of the cost or environmental impacts





Anethole as a Monomer Source

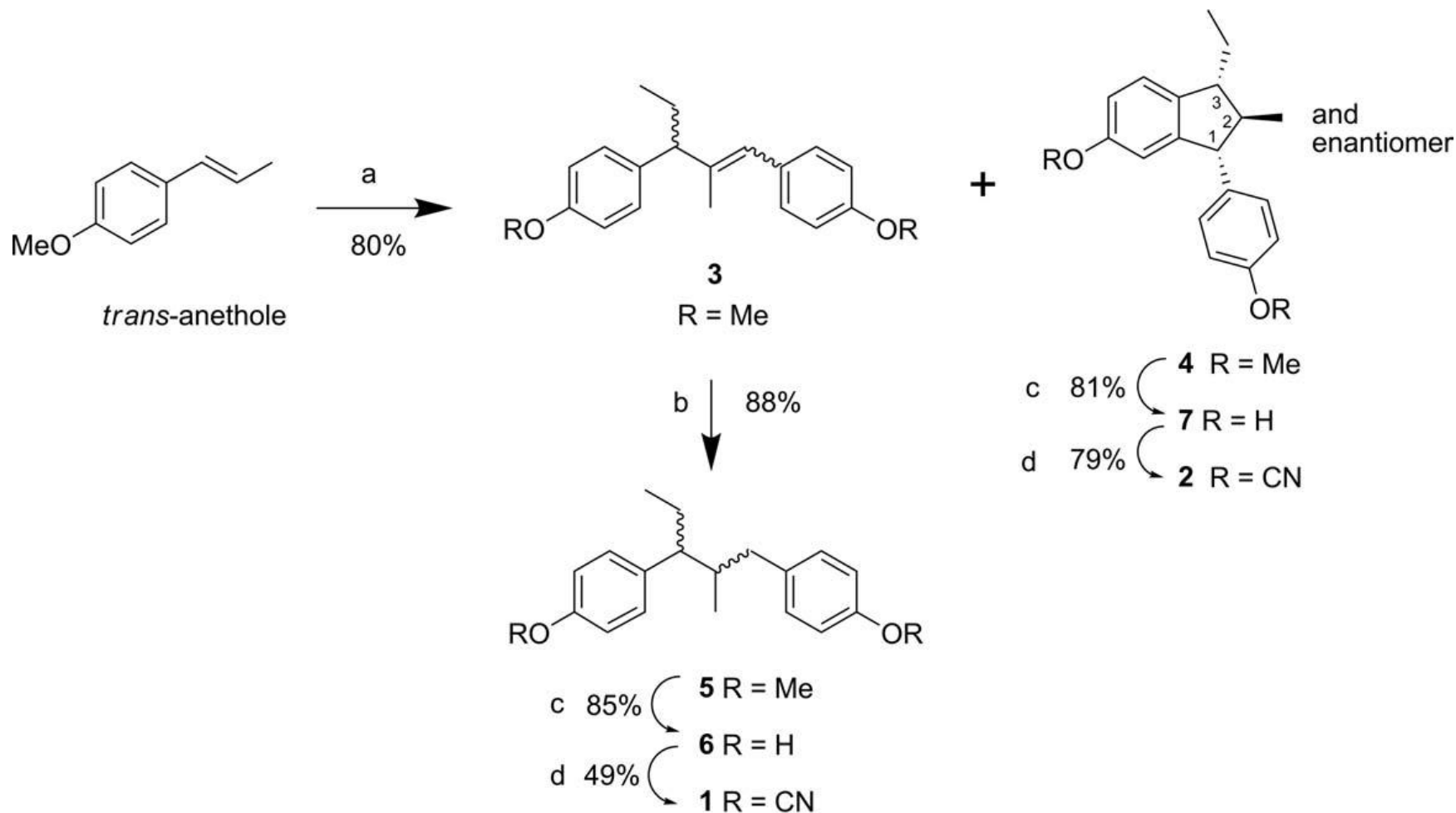


Photograph of fruits of star anise ("Illicium verum"), taken 17th October 2006 by Brian Arthur and released under the GNU Free Documentation License. All remaining rights reserved

- Trans-anethole is widely available as an essential oil extracted from star anise (Illicium verum), an evergreen tree native to southwest China (Yunnan and Guangxi provinces) and northern Vietnam
- Current production is ~ 400 tons / yr, with significant use in the flavor and fragrance industry
- Simple steam distillation of the star anise fruit yields ~90% trans-anethole
- The sizes of the global markets for trans-anethole and cyanate esters are similar



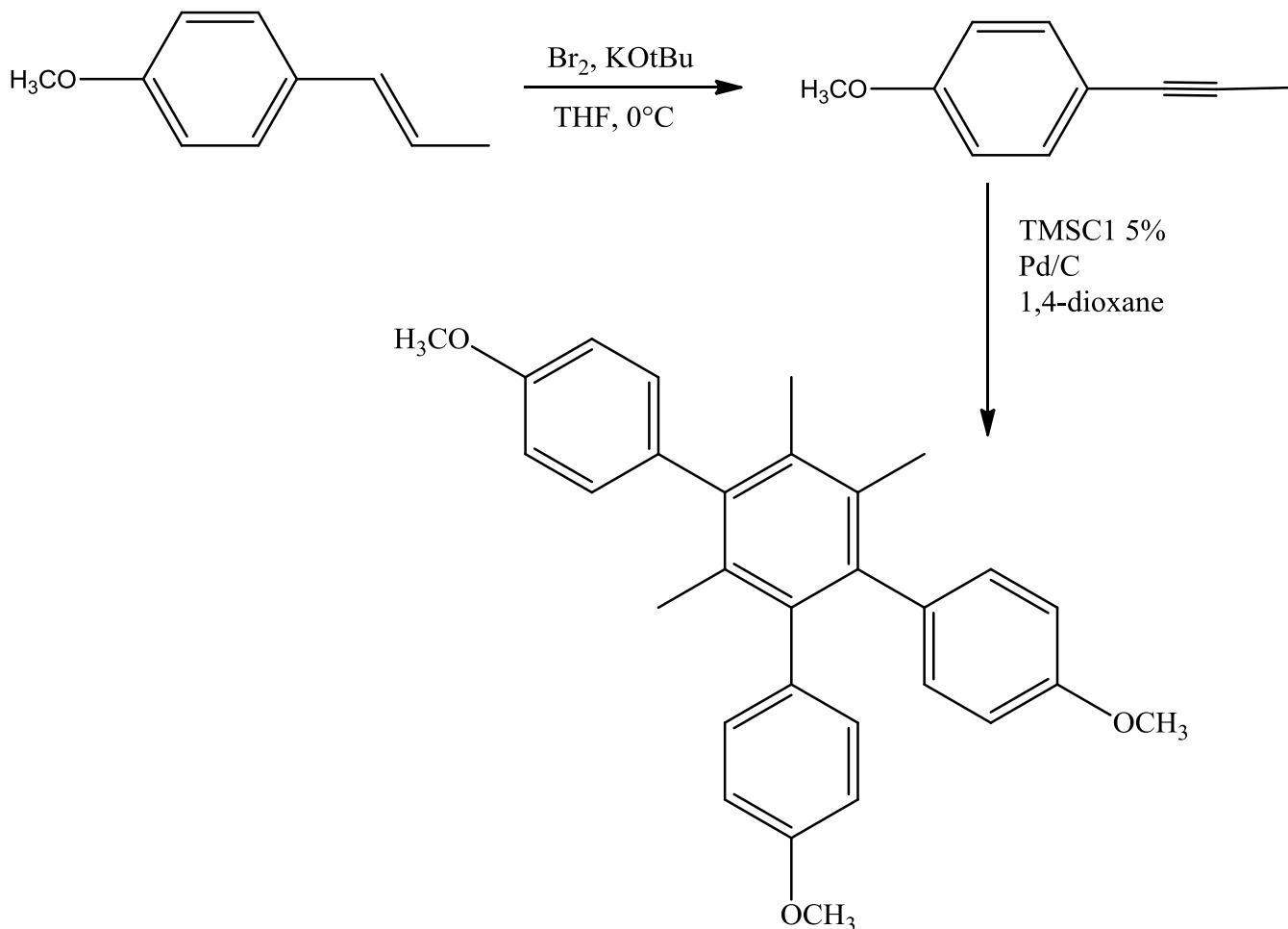
Anethole-Based Cyanate Esters: Route 1



Reagents & conditions: a) H_2SO_4 , H_2O , reflux; b) H_2 , Pd/C, THF; c) pyridineHCl; reflux; d) BrCN, TEA, acetone, -20°C .



Anethole-Based Cyanate Esters: Route 2



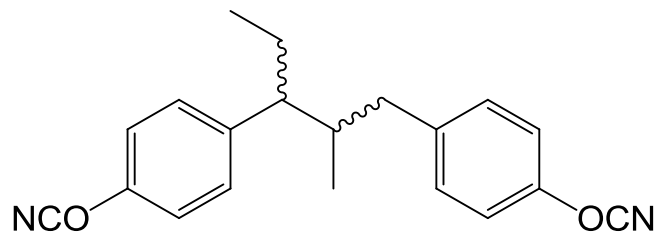
- Final product is a mixture of primarily 1,2,4 and secondarily 1,3,5 isomers. The 1,2,4 isomer was isolated and converted to cyanate ester as in route 1.



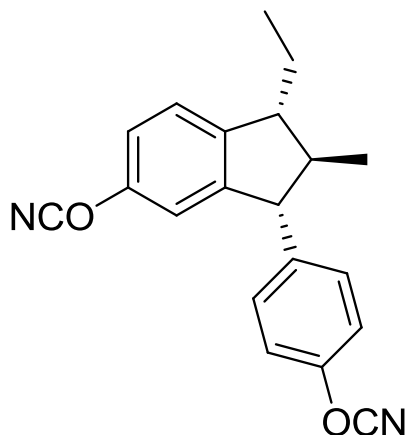
Anethole-Based Cyanate Esters: Range of Segment Flexibility



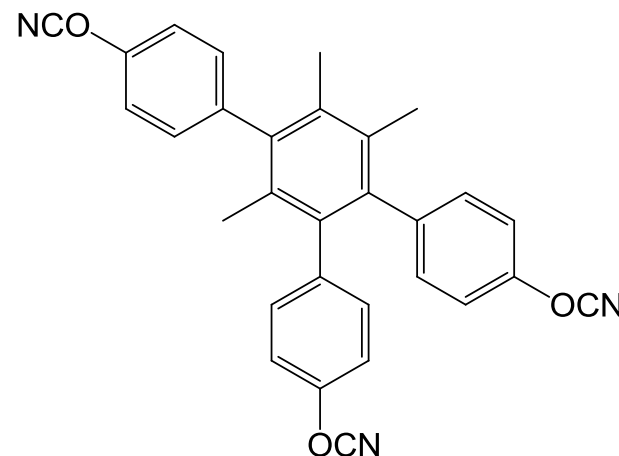
CE-1



CE-2



CE-3



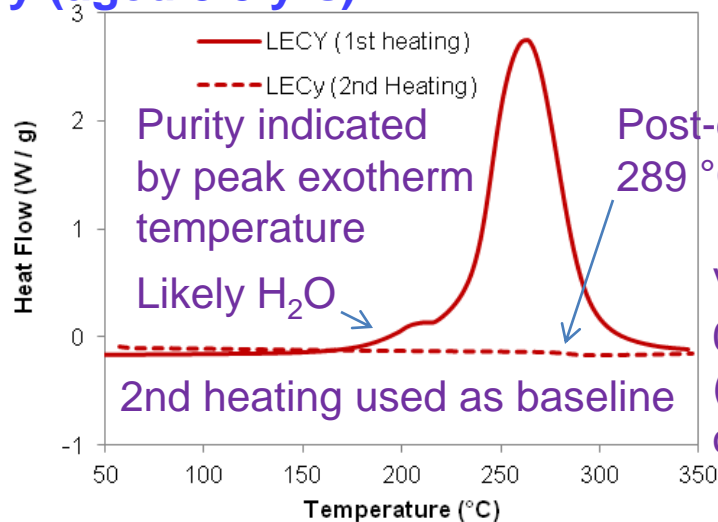
- CE-1 will form networks with a high level of segment flexibility; multiple stereoisomers should inhibit the formation of crystals
- CE-2 will form networks with a moderate amount of segment rigidity
- CE-3 will form highly rigid networks



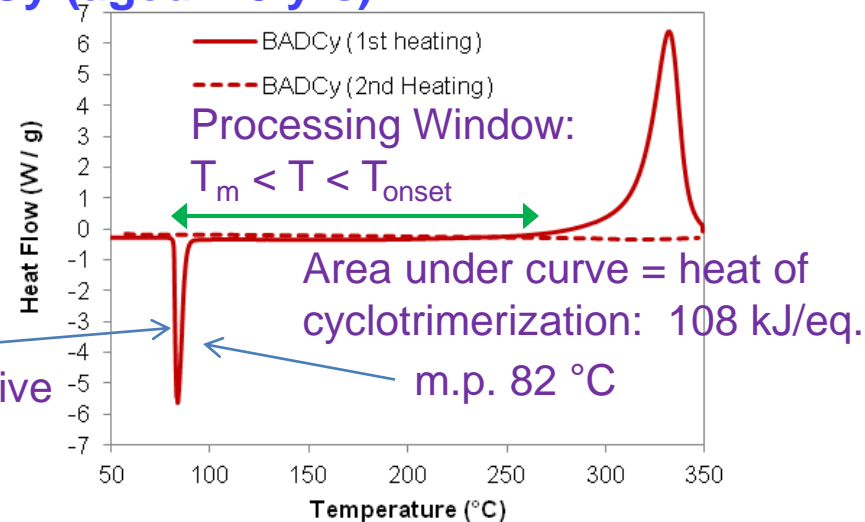
Assessment of Processing Characteristics via DSC



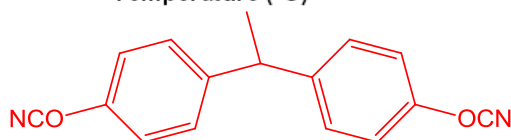
LECY (aged 3.5 yrs)



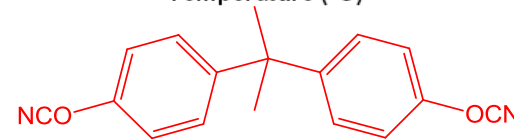
BADCy (aged 2.5 yrs)



LECy



BADCy



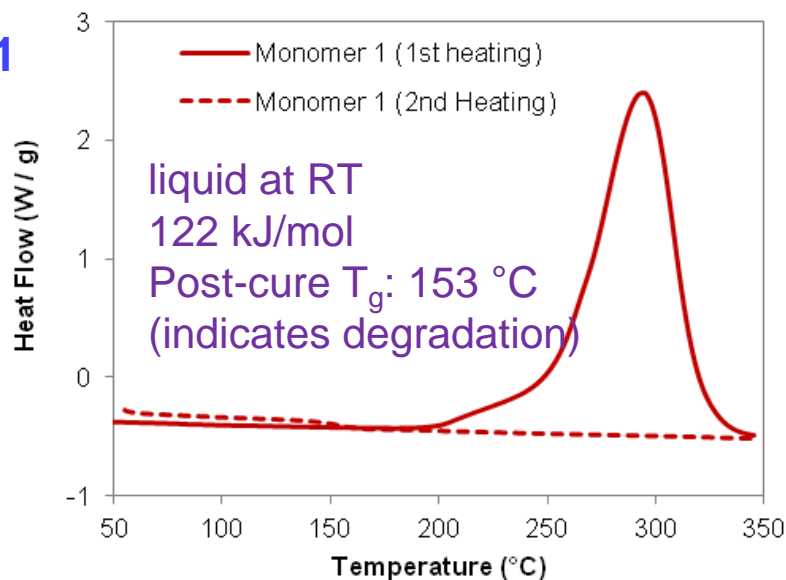
- A non-isothermal DSC scan for cyanate esters reveals many useful processing characteristics
- Highly pure samples should show narrow melting endotherms (if present), exotherm maxima near or above 300 °C, an exotherm of 100 – 110 kJ/eq., relative ease of cure as indicated by a “closed”, symmetric exotherm and appropriate post-cure T_g .
- In this case, a “pot life” study of **uncatalyzed** BADCy and LECy (stored at ambient conditions in the **low humidity** at Edwards AFB) shows no changes in BADCy after 2.5 yrs and only modest contamination of LECy with no significant effects on the final network observed after 3.5 yrs
- Note: Pot life under moderate to high humidity and with catalyst will be much shorter.



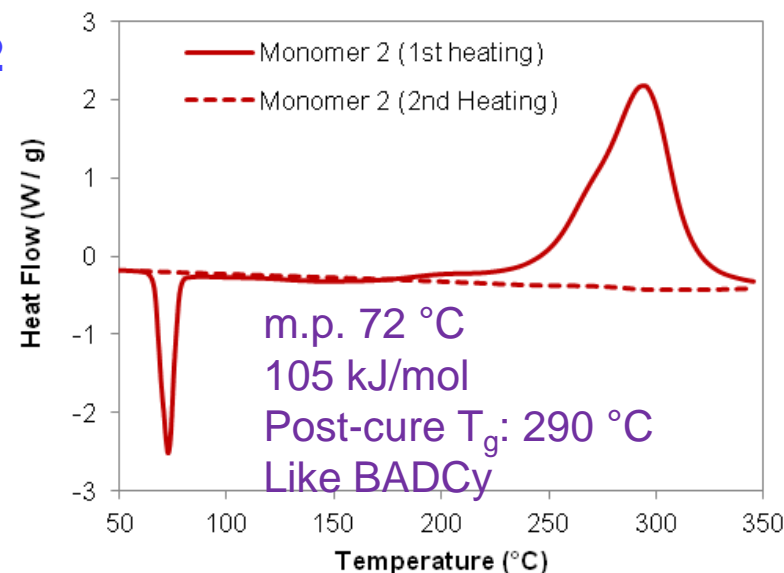
DSC of Anethole-Based Cyanate Esters



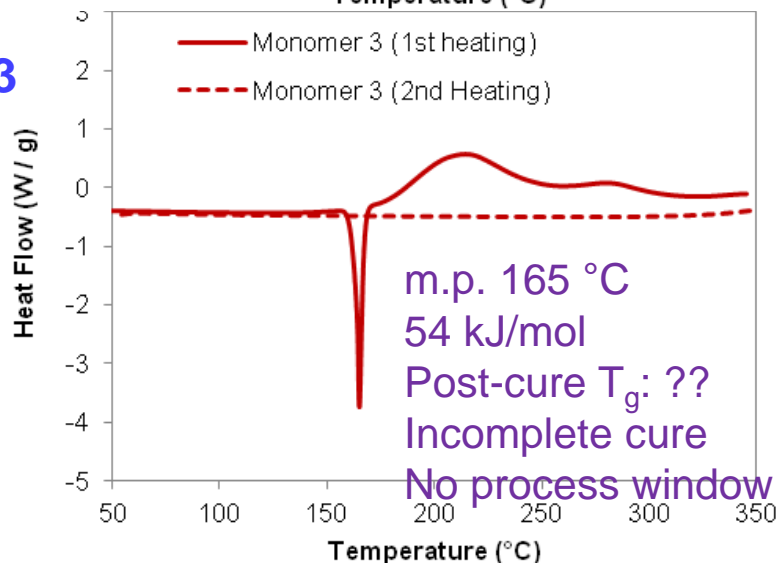
CE-1



CE-2



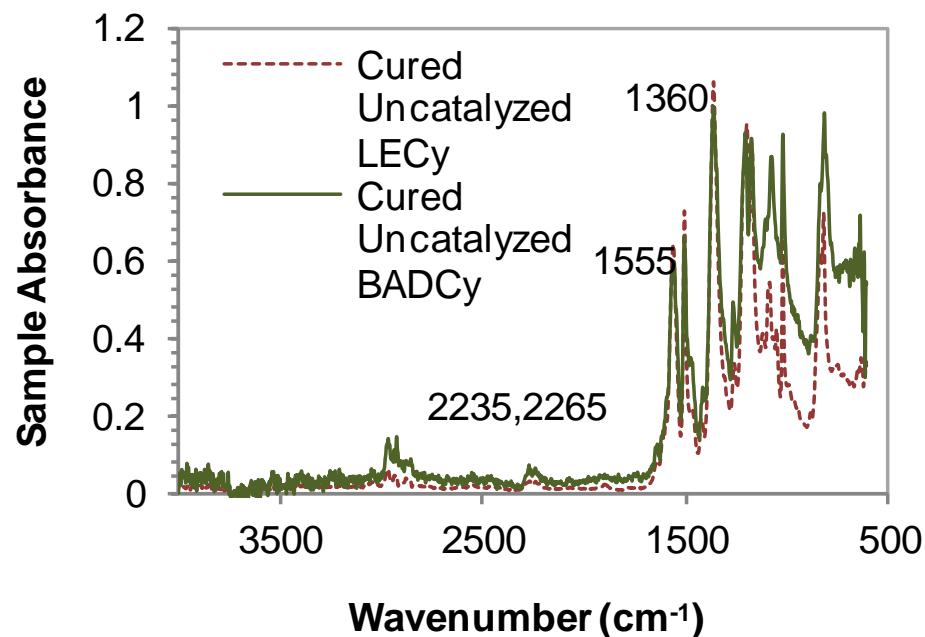
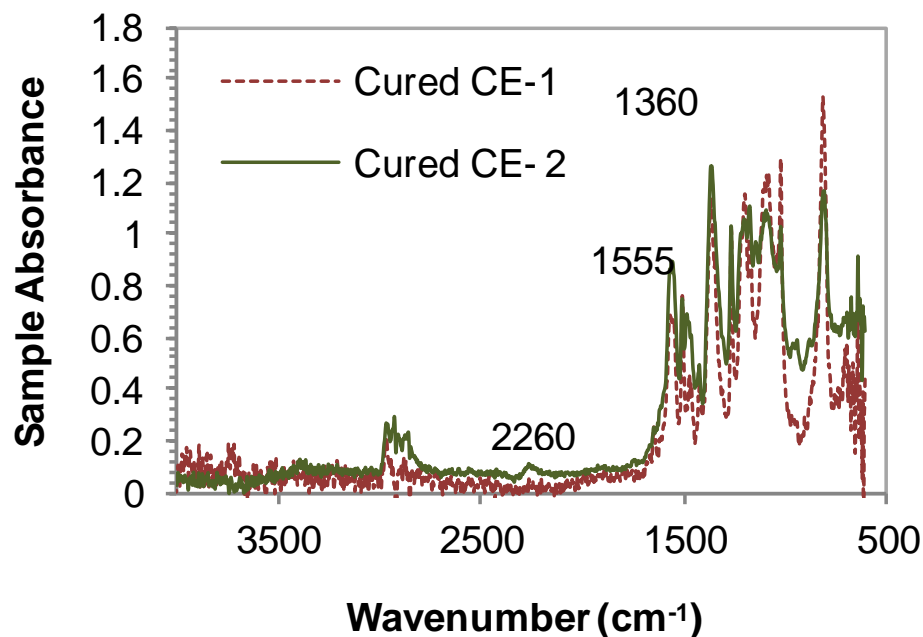
CE-3



- The various coupling routes produce cyanate esters with a wide range of network segment rigidities
- CE-3 (high rigidity) is very difficult to process
- CE-2 has moderate rigidity and is similar in processability to BADCy.
- CE-1 is of low (relative) rigidity, making it the easiest to process



Confirmation of Extent of Cure via FT-IR



Samples cured at 150 °C for 1hr then 210 °C for 24 hrs under dry nitrogen

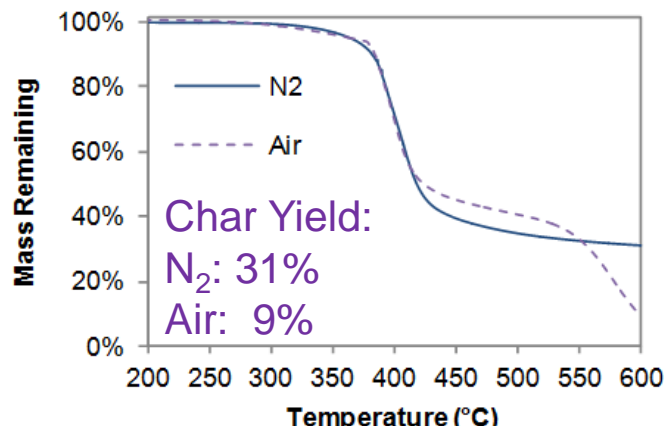
- Similar extent of cure seen in all four samples tested, with slightly lower extent of cure in BADCy and CE-2.
- As expected, the more rigid materials cure less completely. However, this effect may be due, at least in part, to differences in impurity levels.



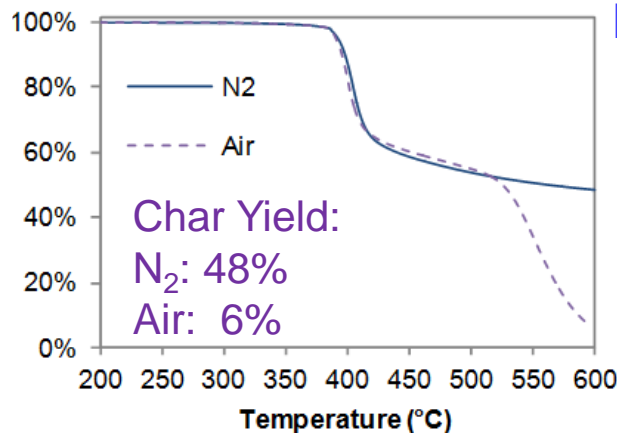
Thermochemical Stability of Anethole-Based Cyanate Esters



CE-1



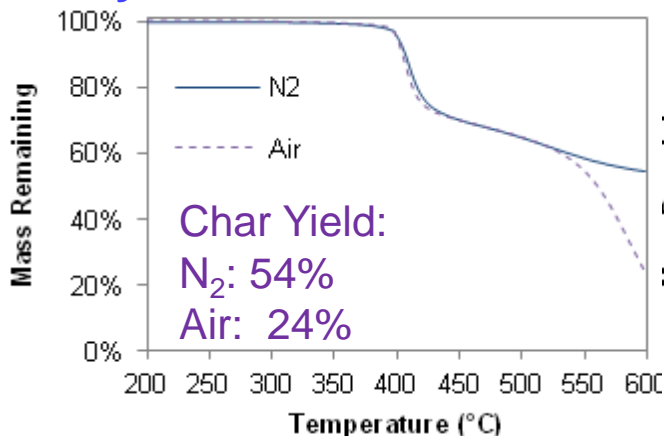
CE-2



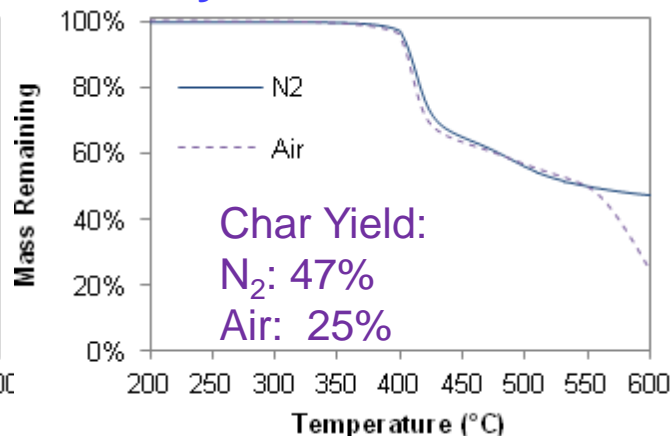
**Network Composition:
Excludes Hydrogen Atoms**

	Wt % Aro- matic	Wt % Aliph- atic	Wt % OCN
CE-1	50	25	25
CE-2	50	25	25
LECy	60	10	30
BAD Cy	57	14	29

LECy



BADCy



Samples cured at 150 °C for 1hr then 210 °C for 24 hrs under dry nitrogen



Physical Properties of Anethole-Based Cyanate Esters



Compound	Density (g/cc)	Cyanurate Density at Full Cure (mmol/cc)	As-Cured Dry T_g by TMA (°C)	T_g After Post-Cure to 350 °C in TMA (°C)	“Wet” T_g After 96 h Immersion in 85 °C H ₂ O (°C)	Water Uptake
CE-1	1.154	2.42	213	223	190	1.14%
CE-2	1.176	2.45	279	313	223	1.66%
LECy	1.231	3.11	291	295	239	1.75%
BADCy	1.208	2.89	275	323	240	1.34%

- In CE-1, water uptake is traded for glass transition temperature (as in RTX-366, which has an even lower water uptake and glass transition temperature)
- CE-2 not only processes like BADCy, but appears to give similar physical properties (though with a slight loss in wet properties)
- Note that the water uptake of LECy and BADCy without catalyst was significantly lower than expected.

LECy (cat)	1.220	3.08	275	290	193	2.34%
BADCy (cat)	1.201	2.86	267	304	186	2.10%

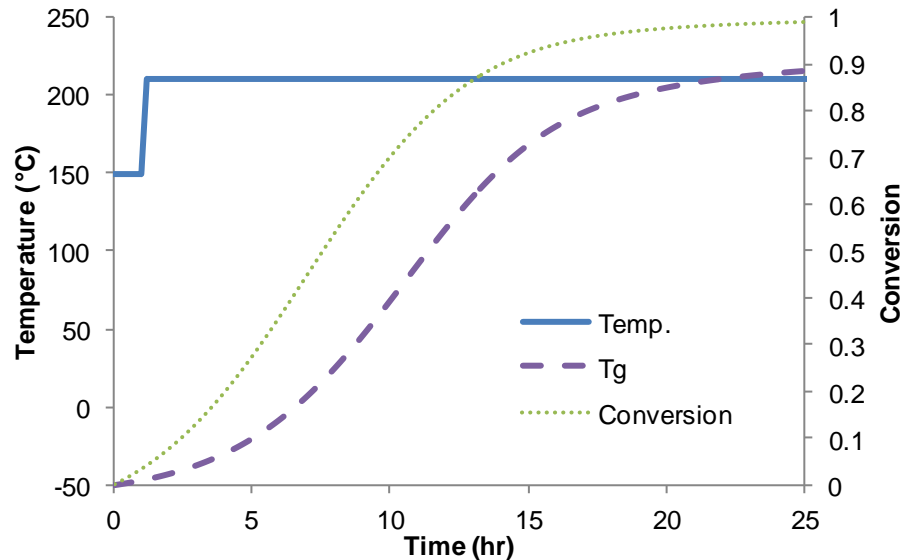
Samples cured at 150 °C for 1hr then 210 °C for 24 hrs under dry nitrogen



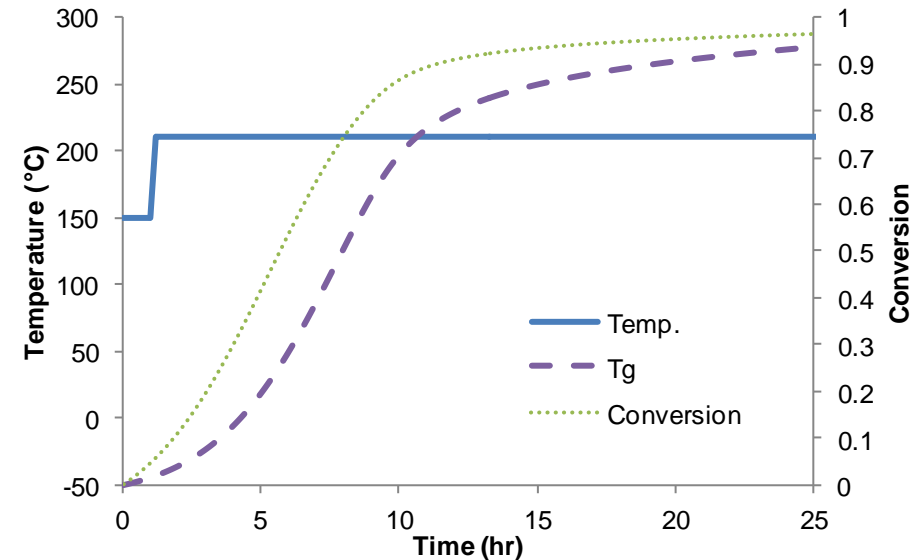
Proposed Relationship Between Water Uptake and Processing



CE-1



CE-2

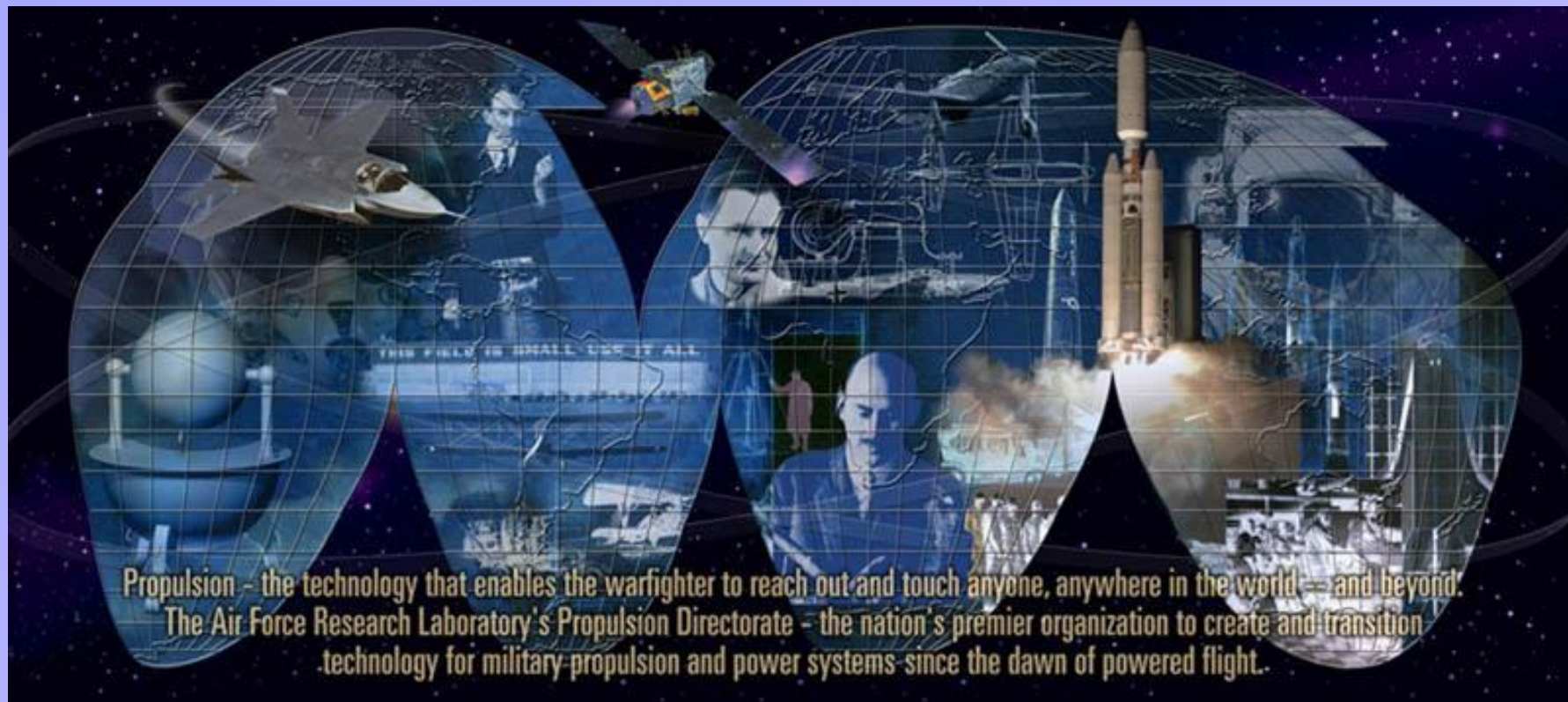


- Though water uptake correlates strongly with cyanurate density, CE-1 has a lower uptake than CE-2 despite having almost the same cyanurate density.
- When $T > T_g$, increased conversion drives down water uptake (initially due to free volume shrinkage, and after the gel point, perhaps due to increasing T_g and/or redistribution of free volume).
- When $T < T_g$, increased conversion increases water uptake due to formation of relatively large free volume regions that are “frozen in”
- The low “as cured” T_g of CE-1 indicates that $T < T_g$ for very little of the cure process, in contrast to CE-2.



Summary / Future Work

- Oxidative coupling of anethole can be used to form cyanate ester monomers that impart a broad range of segment flexibility to cured networks
 - Highly rigid systems exhibited poor processing characteristics and are not being pursued further
 - Moderately rigid system shows processing characteristics and physical properties similar to BADCy, now being scaled up for further investigation
 - Most flexible system is a liquid at room temperature and provides final properties that are intermediate between the commercial products RTX-366 and LECy
 - Due to the higher aliphatic content, the thermo-oxidative stability characteristics of these cyanate esters, though still significantly better than most epoxy resins, did not match those of existing commercial products.
- Areas for future work
 - Since cyanate ester blends often result in networks with synergistic improvements in properties, blending the moderately and highly flexible products from the same oxidation scheme may produce highly desirable combinations of water uptake and glass transition temperature
 - Fabrication of composite panels and, eventually, composite parts incorporating the moderately rigid cyanate ester represents the next step



AFRL

THE AIR FORCE RESEARCH LABORATORY
LEAD | DISCOVER | DEVELOP | DELIVER

